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Polarization dependent ARPES measurements of the valence band structure of anatase TiO_2

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Introduction

Titanium dioxide (TiO_2) has been widely used for the past two decades owing to its technologically promising properties. Regarding photocatalytic activities, anatase TiO_2 is superior to the rutile form. Although a large number of studies have been performed thus far, the fundamental properties of anatase such as the electronic structures of both valence and conduction band regions are less known than those of rutile. Anatase is commercially available in powder form. This is because of the difficulty to synthesize a large-scale single crystal anatase, owing to its less stable form in comparison with the rutile form. In the present study, we have fabricated epitaxial anatase thin films with a good crystallinity and elucidated the valence band structure of the thin films by angle-resolved photoemission spectroscopy (ARPES).

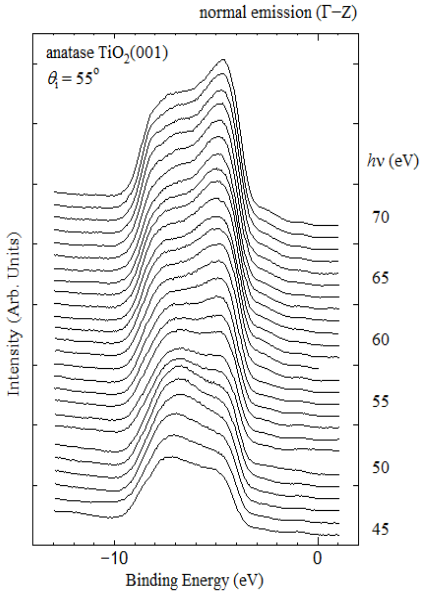
Experiment

Highly oriented anatase films with (001) orientation were epitaxially grown on $LaAlO_3$(100) with an in-plane relationship of [100]anatase//[010]$LaAlO_3$ using pulsed laser deposition with a KrF excimer laser. The ARPES measurements were performed at beam lines 1C and 11D of the Photon Factory, KEK. The valence band structure along the Γ-Z axis was determined from normal emission spectra taken with various photon energies from 45 eV to 70 eV. The synchrotron radiation was linearly polarized in the incidence plane of the light. The spectra were acquired with incidence angles of 20° and 55° (relative to the surface normal direction) so that the ratio of s- and p- polarized components was varied. The spectra were measured at both room temperature and liquid nitrogen temperature.

Results and Discussion

The ARPES spectra show emission structures from the O 2p-dominant valence states between 3 and 9 eV (Fig. 1). The valence states are roughly divided into the non-bonding Pπ states, the π bonding states and the σ bonding states [1]. The emission from Pπ and σ are observed in the ARPES spectra as strong peaks at 4.3 and 7.6 eV, respectively, and there are several peaks recognizable between Pπ and σ. The dispersion relation of the valence states, which is constructed from a series of normal emission spectra, is shown in Fig. 2. We identify seven valence bands, five of which between the shallowest Pπ and the deepest σ bands are newly determined and are associated with the π bands. From the polarization-dependent measurements, π_4 bands, which are observed with the s-polarized light, are mainly composed of the O 2p and Ti 3d orbitals in the (001) atomic plane, whereas π_1, π_2, π_3 and π_5 should be composed mainly of the atomic orbitals out of the (001) plane.

[1] R. Asahi et al., Phys. Rev. B 61, 7459 (2000).



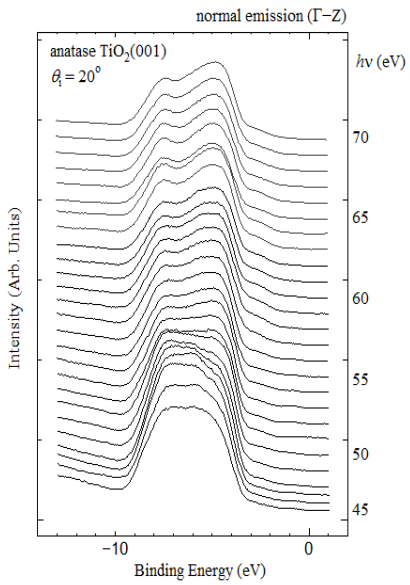


Fig. 1. Normal emission spectra of the anatase TiO_2 (001) surface measured by p-polarized (left) and s-polarized (right) synchrotron light.

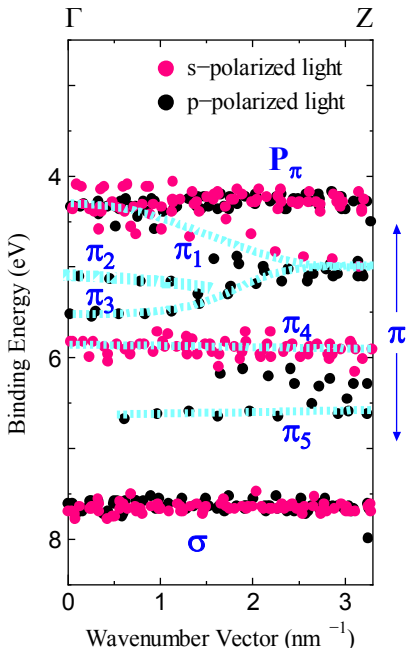


Fig. 2. Valence band structure along the ΓZ axis of anatase TiO_2.